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Persistent Organochlorine Compounds in Sludge and Sediments from the Gdańsk Region, Baltic Sea

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Abstract

Concentrations and profiles of hexachlorocyclohexanes (HCHs), pentachlorobenzene (PCBz), hexachlorobenzene (HCBz), DDT and its metabolites (DDTs), tris(4-chlorophnyl)methane (TCPM-H), tris(4-chlorophnyl)methanol (TCPM-H), chlordane (CHLs), aldrin, dieldrin, isodrin, endrin, endosulfan 1, endosulfan 2, mirex, PCBs and PCNs were determined using isotopically labelled internal standards and HRGC/LRMS in sludge samples collected in 1999 from the sewage treatment plant in Dębogórze (city of Gdynia) and sediment samples taken in 1992 from the Vistula River and Gdańsk Depth in the Baltic Sea. DDT and its metabolites, PCBs, HCBz, dieldrin, CHLs and PCNs were quantified in one to all four samples examined, while PCBz, TCPM-H/OH, aldrin, isodrin, endrin, endosulfan 1 and 2, and mirex were not detected above the detection limit of the method. PCBs dominated among organochlorine compounds quantified in sludge samples while DDTs dominated in the sediment.

Keywords: PCBs, DDTs, CHLs, HCHs, cyclodienes, Dieldrin, TCPM-H/OH, HCBz, PCBz

Introduction

Organochlorine pesticides (OCs) and substances like polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) are man-made compounds which become widespread environmental pollutants and food contaminants on a global scale [1, 2]. These substances have contaminated the Baltic Sea for many years [3-5]. Many of the active ingredients of organochlorine pesticide formulations and their metabolites, as well as congeners of chlorobiphenyl and chloronaphthalene, are very persistent chemicals in the marine environment, and are toxic, bioacumulate and biomagnify in the marine food webs [2, 3, 4, 6].

Because of adverse effects to man and wildlife and persistence in the environment, manufacture, use and trade of organochlorinated compounds has ceased in most countries and new technologies were developed in the 1990s enabling safe disposal of aged pesticide formulations and pesticide wastes as well as wastes, containing PCBs, etc. [7]. The restrictions and bans imposed on persistent organochlorines from the early 1970s has resulted in a decrease in concentration of those chemicals in the marine environment, but at different rates for different matrices and regions of the world in the 1980s-1990s [8-10].

There are many reasons for continuous leakage to and diffusion of man-made, toxic and persistent organochlorine compounds contaminating the environment. Direct sources include outdated pesticide formulations improperly stored or dumped, unofficial or illegal synthesis and further trade and use of formally banned pesticides [11, 12], specific and continuing legal use of organochlorine pesticides (e.g. DDT in reducing the incidence of malaria) [13-15]. Also, improper management of used formula-

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tions, materials, products and/or wastes contaminated with hazardous substances such as PCNs etc. [7]. Many congeners of PCB or PCN are formed and released to the environment during various anthropogenic processes such as incineration, combustion, smelting and metal reclamation [2, 16]. Soil and sediment are secondary sources of many persistent organochlorines which cycle in the biosphere [17, 18].

The Gulf of Gdańsk and Puck Bay are an important economic and ecological resource that receives municipal and industrial discharges mainly via the Vistula (Wisła) River and some local wastewater and stormwater outlets. Untreated municipal sewage from the city of Gdynia until 1994 were discharged directly to the beach zone of Puck Bay in the western part of the Gulf of Gdańsk at the site Mechelinki. From 1994 only well purified municipal effluents are discharged at the Mechelinki site. The Gdańsk Depth is a natural deposition area for fine suspended particulate matter transported via the Wisła River to the Baltic Sea. Municipal and industrial wastewaters are considered major sources of pollutants to river systems and for sediments in near-coastal marine areas. Sludge and sediments, respectively, serve as a reservoir for a variety of potential pollutants, which creates the possibility for aquatic and soil environment degradation.

The number of high quality studies on the occurrence of persistent, toxic and bioaccumulative organic compounds in sludge and sediments in the Baltic south coast region is highly limited [19-22]. This paper reports on the concentrations and profiles of hexachlorocyclohexanes (HCHs), pentachlorobenzene (PCBz), hexachlorobenzene (HCBz), DDT and its metabolites (DDTs), tris(4-chlorophnyl)methane (TCPM-H), tris(4-chlorophnyl)methanol (TCPM-H), chlordane (CHLs), aldrin, dieldrin, isodrin, endrin, endosulfan 1, endosulfan 2, mirex, PCBs and PCNs in sludge samples collected in 1999 and sediment samples taken in 1992 from the region of the Gulf of Gdańsk.

Materials and Methods

Sewage sludge samples were collected from the Dębogórze sewage treatment plant (Oczyszczalnia Dębogórze) in the vicinity of the city of Gdynia in spring 1996. Sludge samples were collected separately from two sludge fermentation tanks after primary treatment. From each tank six 0.5 kg individual samples were collected, which were further well mixed to compose pooled sample. One surface sediment sample (0-10 cm) was collected by hand using steel less spatula from the Vistula River at the site Kiezmark (near the city of Gdańsk, Voivodeship Pomorskie) from the depth of ~0.5 m and about 5 meters from the shore-line, and one from the depth of 97 m in the Gdańsk Depth (N 54° 43´; E 19° 14´) in the Baltic Sea in 1992 during r/v Oceania cruise and using a large size professional bottom sediment sampler (Figure 1). The samples after collection were placed in clean polythylene

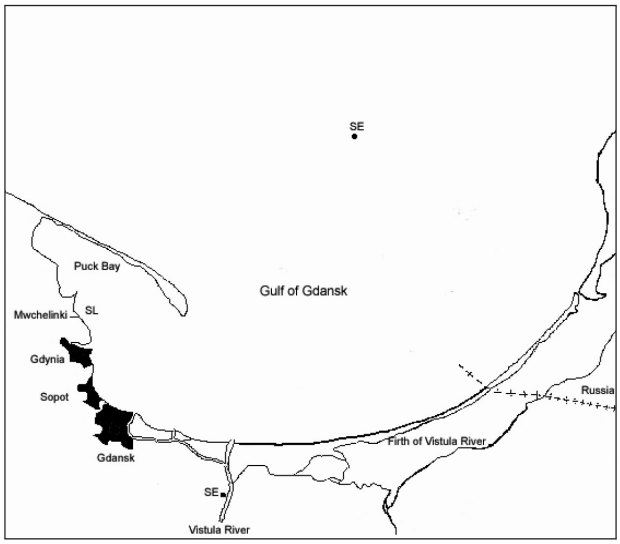

Fig. 1. Location of the sampling sites (SL, sludge and SE, sediments).

bags and deep frozen (- 20°C) until analysis. Next, the samples were air dried in clean condition in room temperature and homogenized. A sub-sample was taken to determine dry matter content after heating at 100°C in electrically heated oven until sample constant weight.

The analytical method used for the quantification of organochlorine pesticides, PCBs and PCNs have been described elsewhere [23]. Briefly, 10-11 g sub-sample was extracted wet in a Soxhlet Dean Strak apparatus with toluene (200 ml for 24 hours) and a mixture of n-hexane and acetone (59:41, v/v; 24 hours). Bulk lipid removal was performed by means of the polyethylene film dialysis method. After dissolving the extracted lipids in cyclopentane, dialysis through the polymeric membrane was accomplished by changing the dialysate after 24, 48 and 72 h [23]. The extract was split into two parts, of which 10% was used for analysis of organochlorine pesticides and PCBs. This fraction was finally cleaned-up on a Florisil column. Before extraction step an internal standard mixture containing numerous $^{13}C_{12}$ - labelled and deuterated compounds was added, including $^{13}C_{12}$ - DDT, dieldrin, PCB no. 80 and PCB no. 153. Analysis and detection was performed using high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS). The MS instrument was a Fison MD 800 operating in the Electron Impact (EI) mode using ion recording (SIR). The GC was a Fisons GC 800 with DB-5 (60 m x 0.32 mm I.D. and 0.25 μm film thickness) column. In the case of organochlorine pesticides quantification was performed against external standard containing, except some of the minor constituents of technical chlordane, all compounds determined in this study, while in the case of PCBs against one PCB congener for each homologue group. The reported concentrations were corrected for the recovery rates. Since the analytical

Table 1. Organochlorine pesticides, PCBs and PCNs (ng/g d. w.) in sludge and sediments from the Gdańsk region, Baltic Sea.

Compound	Sludge[#]		Sediment	
	Dębogórze 1	Dębogórze 2	Vistula River	Gdańsk Depth
HCHs	ND (<0.5)	ND (<0.5)	ND (<0.1)	ND (<0.1)
PCBz	ND (<0.3)	ND (<0.3)	ND (<0.05)	ND (<0.05)
HCBz	8.6	11	4.7	0.93
DDTs	330	490	77	15
TCPM-H/OH	ND (<1.7)	ND (<1.7)	ND (<0.3)	ND (<0.3)
CHLs	4.0	4.1	0.13	ND (<0.7)*
Dieldrin	8.6	9.9	ND (<0.20)	ND (<0.20)
Aldrin	ND (<0.8)	ND (<0.8)	ND (<0.15)	ND (<0.15)
Endrin	ND (<0.8)	ND (<0.8)	ND (<0.15)	ND (<0.15)
Isodrin	ND (<6.7)	ND (<6.7)	ND (<1.2)	ND (<1.2)
Endosulfan 1, 2	ND (<17)	ND (<17)	ND (<3)	ND (<3)
Mirex	ND (<1.7)	ND (<1.7)	ND (<0.3)	ND (<0.3)
PCBs	650	370	5.6	1.2
PCNs	NA	NA	6.7	NA

[#]Loss on ignition (LOI) - 41.5% and 44.4%, respectively; ND (not detected); NA (not analysed); *from <0.04 to <0.12 ng/g d. w. for the main chlordane constituents.

method used was validated for several occasions [23] and isotopic labelled internal standards were used, no replicates were made.

Results and Discussion

DDT and its metabolites, PCBs, HCBz, dieldrin, CHLs and PCNs were quantified in one to all four samples examined (Table 1), while PCBz, TCPM-H/OH, aldrin, isodrin, endrin, endosulfan 1 and 2, and mirex were not detected above the detection limit of the method. To our knowledge reports on concentration of many groups of organochlorine pesticides in sewage sludge from the region of the Gulf of Gdańsk are not available. A recent study has reported the occurrence of PCBs in sludge from the sewage treatment plant in the city of Gdańsk [21]. Concentrations of PCBs in dried sludge from the Oczyszczalnia Wschód sewage treatment plant in Gdańsk ranged between 130 and 370 ng/g and there was no significant reduction of concentration after primary treatment in open sludge fermentation tank. In this study concentrations of PCBs in sludge (Table 1) were between 370 and 650 ng/g dry wt., i.e. twice that of the sludge from the city of Gdańsk. Polychlorinated biphenyls dominated among organochlorine compounds quantified in sludge samples while DDT and its metabolites dominated in the sediment samples. Elevated concentrations of PCBs in sludge when compared to sediments suggest that until the year 1994 unpurified wastewater discharged from the Dębogórze sewage treatment plant could be an important local source of PCB pollution in Puck Bay. There is not a major differences in profile of chlorobiphenyl congeners between sludge collected from two different sludge fermentation tanks and a large difference is for the sediment samples (Fig. 2). The surface sediments collected from the deep of 97 meters in the Gdańsk Depth area are evidently aged with hexa-CBs (64%), hepta-CBs (25%) and penta-CBs (11%) as major homologue groups. Contrary to the PCBs profile from the Vistula River, sediments seem to reflect fresh inputs with a relevant load of lower chlorinated congeners (30% of tetra-CBs and 14% of penta-CBs). The profile of PCBs in sediments from the Vistula River is consistent with that found in flounder caught close to the outlet of the Vistula River, and which contained in a large proportion lower chlorinated congeners of chlorobiphenyl – tri- (4%), tetra- (18%) and penta-CBs (25%) but was different from that of other biota in the southern part of the Baltic proper [24, 25]. Nevertheless, PCBs were quantified in sediments from the Vistula River in a small concentration (Table 1), and also a small amount of PCBs is transported via the Vistula river (5.0 kg annually in 1991-92) [26].

DDTs are next to PCBs as dominating compounds in sludge. The profile of DDTs in sludge samples is very similar and the same can be found for sediments, respectively, but there are large differences between those two matrices with p,p′ - DDT and p,p′ - DDE abundant in sediment (Fig. 3). In anaerobic conditions p,p′- DDT is transformed mainly to p,p′ - DDD, while in aerobic to

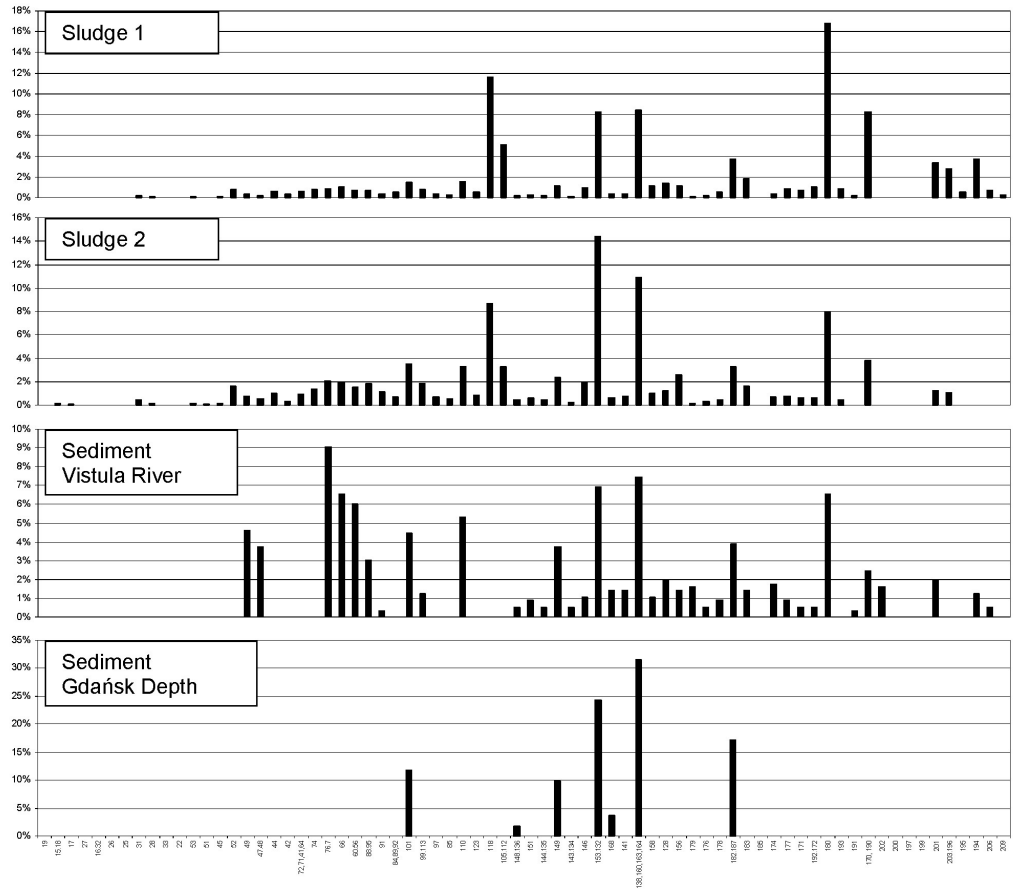

Fig. 2. Profile (%) of PCBs.

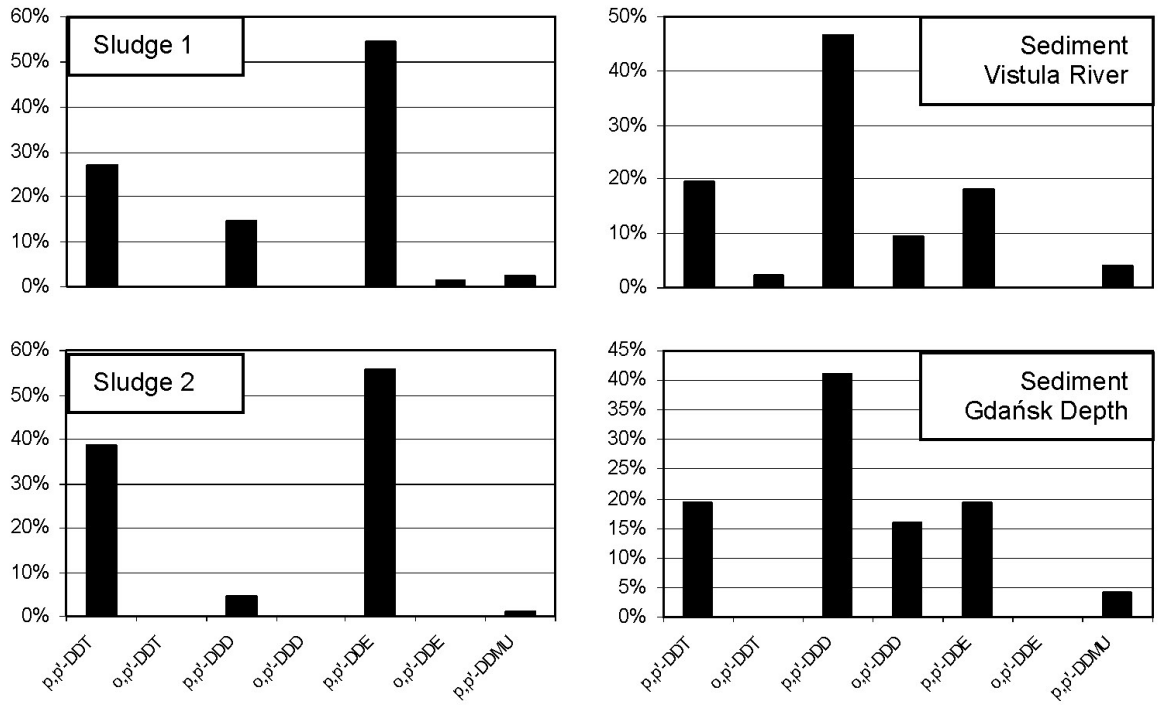

Fig. 3. Profile (%) of DDTs.

p,p′ - DDE [27, 28]. There is also a possibility of anaerobic transformation of p,p′ - DDE to p,p′ - DDMU [18]. A similarity of DDT profiles between the sediments from the Vistula River and Gdańsk Depth suggest a common origin of those compounds. A dominating role of the Vistula River as a possible source of particle bound DDTs washed-out from the top soil horizon at the river drainage area and their further transport/relocation towards the Gdańsk Depth. A similar picture can be drawn from the values of p,p′ - DDT to p,p′- DDE quotient in sludge (between 0.50 and 0.64) and sediments (between 1.0 and 1.1). A value of p,p′ - DDT to p,p′ - DDE quotient above 1 suggest on relatively fresh source of DDT. Since p,p′ - DDT relatively firmly bounds to soil particles and is very persistent in soil a noted 1.1 value of quotient for p,p′ - DDT to p,p′ - DDE in sediments implies on mostly terrygenic source of those compounds in the Vistula River.

Dieldrin, hexachlorobenzene and chlordanes are a minor organochlorinated constituent both in the sludge and sediment samples (Table 1), and HCBz seems to be more common than dieldrin and CHLs. Trans-nonachlor to cis-chlordane quotient (N/C ratio) in sludge samples is between 1.1 and 2.1, which implies on aged residues since in technical chlordane the N/C ratio is around 0.36. Polychlorinated naphthalenes (PCNs) were quantified only in sediments from the Vistula River and surprisingly were found in similar concentration to PCBs.

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